

OZONE PRODUCTION IN URBAN PLUMES

Lawrence Kleinman
Atmospheric Sciences Division
Brookhaven National Laboratory
Upton, NY 11973-5000

August 2001

Submitted for inclusion in
Proceedings of 10th International Symposium
"Transport and Air Pollution"
Boulder, CO
Sept. 17-19, 2001

Abstract

Using data collected from the DOE G-1 aircraft during field campaigns in Phoenix, Philadelphia, and Houston, we examine the process of O₃ production in urban plumes. Ozone levels in Houston are significantly higher than in Phoenix or Philadelphia. We find that comparable amounts of NO_x are processed in each city but that the O₃ production efficiency in Houston (molecules of O₃ formed per NO_x molecule consumed) is 2 to 3 times higher than in Phoenix or Philadelphia. Constrained steady state box model calculations show that the higher efficiency in Houston is due to a higher VOC to NO_x – OH reactivity ratio. Reactive olefins from the petrochemical complex in the Houston ship channel region contribute towards the higher reactivity ratio in Houston.

Keywords: Ozone, ozone production efficiency, photochemical calculation

Introduction

Over the past 4 years the DOE Atmospheric Chemistry Program has conducted photochemical field programs in several large urban areas, including Phoenix (May-June 1998), Philadelphia (July-August, 1999), and Houston (August-September, 2000). Our strategy has been to study O₃ production in a diverse range of environments and to exploit differences between these environments to further our understanding of the overall O₃ formation process. In each city the DOE G-1 aircraft was used to measure O₃, CO, VOCs, NO, NO₂ (except Philadelphia), NO_y, HCHO, SO₂, and peroxides. These observations are part of a larger data set that includes surface sites and other aircraft platforms. For a description of the scope of the field campaigns in Phoenix, Philadelphia, and Houston see Fast et al (2000), Philbrick et al (2000), and the Texas Air Quality Study web page (www.utexas.edu/research/ceer/txaqs/), respectively.

Ozone levels in Houston were much higher than Phoenix or Philadelphia. Eight flights spread over 7 days encountered peak O₃ concentrations between 150 and 211 ppb. Maximum O₃ in Phoenix and Philadelphia were 101 and 147 ppb, respectively. We ascribe the high O₃ levels in Houston to an efficient utilization of NO_x, ie a high ozone production efficiency (OPEX). This quantity is defined as the number of molecules of O₃ formed per NO_x molecule converted to oxidation products. Figure 1 illustrates one method of determining OPEX, as a slope of a graph of O_x (O₃+NO₂) vs. NO_z (Trainer et al, 1993). NO_z is the sum total of all NO_x oxidation products determined as the difference between NO_y (total odd nitrogen) and NO_x (NO+NO₂), ie NO_z = NO_y-NO_x. Figure 1 shows that photochemistry has produced comparable amounts of NO_z in Phoenix and Houston, but that O_x levels in Houston are more than double that in Phoenix because the photochemistry uses NO_x much more efficiently. There is day to day and place to place variability in OPEX according to the type of plume and its processing conditions. Representative values for Houston, Phoenix, and Philadelphia are OPEX = 7-12, 3, and 4, respectively.

Calculations

Aircraft based observations have been used as input to a constrained steady state (CSS) box model (Kleinman et al, 1997). The limiting factor in doing CSS calculations is, in general, the availability of VOC data which is collected in canisters and analyzed by J. Rudolph's research group at York University. CSS calculations have been done at over a 100 sampling points in Phoenix and Philadelphia and over 200 in Houston. The calculations yield the concentrations of free radicals; the O₃ production rate, P(O₃); and the rate of NO_x oxidation equal to the production rate of NO_z, P(NO_z). The ratio of P(O₃) to P(NO_z) is the number of molecules of O₃ produced per NO_x molecule at the time and place that the calculation is performed. This quantity is an instantaneous analog of OPEX.

Equation (1) is a steady state analytic formula for P(O₃)/P(NO_z) similar to that derived by Derwent and Davies (1994), Daum et al (2000) and Carpenter et al (2000):

$$P(O_3)/P(NO_z) = \sum Y_i k_i [VOC_i]/k_N [NO_2] \quad (1)$$

where the k_i's are rate constants for reaction of VOC_i with OH, k_N is the rate constant for OH +NO₂, and Y_i is the number of peroxy radicals produced from reaction of OH with a VOC as determined from the stoichiometry of the reaction. VOCs are broadly defined to include all substance which react with OH producing a peroxy radical. In Fig. 2 we test our analytic formula by comparing values of P(O₃)/P(NO_z) obtained from CSS calculations with that obtained from Eq. (1). For this purpose we have used calculations based on the Phoenix data set. There is seen to be qualitative agreement as long as NO_x concentrations are greater than 1 -2 ppb. Figure 2 also shows that P(O₃)/P(NO_z) increase at low NO_x concentration in agreement with the work of Liu et al (1987) and Lin et al (1988).

Figure 3 shows a comparison between P(O₃)/P(NO_z) for Houston, Philadelphia, and Phoenix. Again we see the expected increase at low NO_x concentration. At NO_x levels greater than a few ppb, where most of the O₃ is formed the instantaneous P(O₃)/P(NO_z) for Houston is greater than Philadelphia which is greater than Phoenix. This variation is in the right direction and of the right magnitude to qualitatively explain the observed city to city differences in OPEX.

According to (1), P(O₃)/P(NO_z) depends on a VOC to NO₂ - OH reactivity ratio. This leads us to look at VOC reactivity as a possible cause for high OPEX. All three cities are large and have the attendant pollution problems due to mobile sources. In Phoenix, mobile sources are the predominant emission source (Heisler et al. 1997), less so in

Philadelphia, and still less so in Houston. There is a very large concentration of petrochemical facilities in Houston near the ship channel just east of the city center. Most of the high $P(O_3)/P(NO_x)$ data points in Fig. 3 are due to samples collected in this region. There is a subset of ship channel samples containing 10's of ppb of ethene and propene. These concentrations are an order of magnitude more than expected for vehicular emissions, based on VOC measurements by W. Lonneman in the Houston Washburn Tunnel.

Conclusions

Ozone levels observed during a field campaign in Houston were significantly higher than that observed in Phoenix or Philadelphia. An examination of the slope of O_x versus NO_x in the urban plumes shows that NO_x is used 2 to 3 times more efficiently in Houston as compared with Phoenix and Philadelphia. Representative values of OPE_x are 7-12, 3, and 4, in Houston, Phoenix, and Philadelphia. Aircraft observations have been used to calculate $P(O_3)/P(NO_x)$. Values in Houston are significantly higher than in Phoenix and Philadelphia. We show that $P(O_3)/P(NO_x)$ is proportional to a $VOC/NO_2 - OH$ reactivity ratio. High values of $P(O_3)/P(NO_x)$ in Houston are due to emissions of reactive olefins from the ship channel region. It is significant that high values of $P(O_3)/P(NO_x)$ occur at NO_x levels up to several 10's of ppb. Not only is the chemistry efficient but it will be long lasting. The occurrence of high NO_x and high OPE_x is fostered by the co-location of VOC and NO_x sources in the Houston industrial areas.

References

- Carpenter, L.J., T.J. Green, G.P. Mills, S. Bauguette, S.A. Penkett, P. Zanis, E. Schuepbach, N. Schmidbauer, P.S. Monks, and C. Zellweger, Oxidized nitrogen and ozone production efficiencies in the springtime free troposphere over the Alps, *J. Geophys. Res.* **105**, 14,547-14,559, 2000.
- Daum, P.H., L.I. Kleinman, D. Imre, L.J. Nunnermacker, Y.-N. Lee, S.R. Springston, L. Newman, J. Weinstein-Lloyd, R.J. Valente, R.E. Imhoff, R.L. Tanner, and J.F. Meagher, Analysis of O_3 formation during a stagnation episode in Central TN in Summer 1995, *J. Geophys. Res.*, **105**, 9107-9120, 2000.
- Derwent, R.G., and T.J. Davies, Modelling the impact of NO_x or hydrocarbon control on photochemical ozone in Europe, *Atmos. Environ.*, **28**, 2039-2052, 1994.
- Fast, J.D., J.C. Doran, W.J. Shaw, R.L. Coulter, and T.J. Martin, The evolution of the boundary layer and its effect on air chemistry in the Phoenix area, *J. Geophys. Res.* **105**, 22,833-22,848, 2000.
- Heisler, S.L., P. Hyde, M. Hubble, F. Keene, G. Neuroth, M. Ringsmuth, and W.R. Oliver, Reanalysis of the Metropolitan Phoenix early ozone plan (VEOP), ENSR Document 0493-014-710, Oct., 1997.
- Kleinman, L.I., P.H. Daum, J.H. Lee, Y.-N. Lee, L.J. Nunnermacker, S.R. Springston, L. Newman, J. Weinstein-Lloyd, and S. Sillman, Dependence of ozone production on NO and hydrocarbons in the troposphere, *Geophys. Res. Lett.*, **24**, 2299-2302, 1997.
- Lin, X., M. Trainer, and S.C. Liu, On the nonlinearity of the tropospheric ozone production, *J. Geophys. Res.* **93**, 15,879-15,888, 1988.
- Liu, S.C., M. Trainer, F.C. Fehsenfeld, D.D. Parrish, E.J. Williams, D.W. Fahey, G. Hübner, and P.C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res.* **92**, 4191-4207, 1987.
- Philbrick, C.R., R.D. Clark, P. Koutrakis, J.W. Munger, B.G. Doddridge, W.C. Miller, S.T. Rao, P. Geogopoulos, and L. Newman, Investigations of ozone and particulate matter air pollution in the northeast, *PM2000: Particulate Matter and Health – The scientific basis for regulatory decision making*, Air and Waste Management Assoc., Charleston, SC Jan 2, 2000.
- Trainer, M. et. al., Correlation of ozone with NO_y in photochemically aged air. *J. Geophys. Res.* **98**, 2917-2925, 1993.



